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pH-Dependent reversible crystal transformation of 1-carboxymethyl-1-methyl-pyrrolidinium bromides and their spectroscopic fingerprint

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ABSTRACT

In this work, two 1-carboxymethyl-1-methyl-pyrrolidinium bromides (*N*-methylpyrrolidine betaine hydrobromides) with the stoichiometry of betaine:hydrobromic acid as 1:1 and 2:1, denoted as CMPRHBr-I and CMPRHBr-II, respectively, were prepared and crystallographically determined. The large difference in these two structures is the type of hydrogen bonds, resulting in the different thermal stability. A strong O—H···Br hydrogen bond was observed in CMPRHBr-I, whereas O···H···O hydrogen bond in CMPRHBr-II. Both these two crystals can mutually transform by changing the pH value of the aqueous solution. Vibrational spectroscopic studies shows that these two structures can be easily distinguished by the characteristic bands such as νC═O stretching vibration and the D-type bands. Our studies indicate that it should be cautious of the structural change as this type of organic salts was purified and recrystallized.

1. Introduction

Organic salts are frequently used as ionic liquids [1], catalysts [2], conductive electrolytes [3] and other special chemicals [4,5]. Amongst them, betaines, generally including all the internal quaternary ammonium, phosphonium and sulphonium salts [6] are essential substances for the synthesis of amino acids, peptides, proteins and nucleosides, and also play an important role in animal and plant tissues [7]. These salts often crystallize in different forms due to the various hydrogen bonds. For example, Dega-Szafran and co-workers [8–11] have carried out a series of studies to achieve crystal structures and hydrogen bond types of pyrrolidinium, piperidinium, imidazolium. They found that the hydrogen bonds of these salts are mainly classic O—H···N, O···H···O, O—H···X (Cl^-, Br^-, O) and weak C—H···X interactions. In fact, these hydrogen bonds are very important for the biological processes involving rapid association and dissociation, and can directly affect their physical-chemical properties. However, there is little information on the relation between different hydrogen-bonded structures and on whether they can mutually convert or not.

The recently prepared carboxyl-functional pyrrolidinium has been used as an ionic liquid to selectively dissolve the metal oxides [12], and also considered to be used in catalysis, organic synthesis, liquid/liquid extraction and combustion chemistry [13–15]. Due to the coexistence of carboxyl group and quaternary ammonium, its property can be tailored by the simple modification of the side chain and by changing the anion. However, it should be careful during the purification and recrystallization since they can crystallize in different forms for the sake of the various types of hydrogen bonds between COOH groups and anions [10,12,16].

In our previous work, we reported the crystal structures of COOH-functionalized imidazolium chloride [17] and its zwitterion [18], and found the difference in hydrogen bonds. As a continuation of our crystal structural studies, we focus our attention on the 1-(carboxymethyl)-1-methylpyrrolidinium bromide, despite its structure has been analyzed by IR, ^{1}H and ^{13}C NMR spectra [19], because we believe that it can crystallize in other form. During the purification and recrystallization we obtained indeed two different crystal structures. Interestingly, they can mutually convert only by adjusting the pH value of the solution. The

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Table 1
Crystal data and structure refinement for CMPRHBr-I and CMPRHBr-II.

(CMPR·HBr)-I	(CMPR·HBr)-II
$C_5H_{11}N^+CH_2COOH\cdot Br$	$[C_5H_{11}NCH_2COO\cdot H\cdot OOCCH_2NC_5H_{11}]^+Br$
$C_7H_{14}BrNO_2$	$C_{14}H_{27}BrN_2O_4$
MW = 224.10 g/mol	MW = 367.29 g/mol
T = 296 K	T = 296 K
λ = 0.71073 Å	λ = 0.71073 Å
Orthorhombic	Monoclinic
$P2_12_12_1$	C2/c
$a = 7.0124(17)$ Å $\alpha = 90°$	$a = 11.867(10)$ Å $\alpha = 90°$
$b = 10.868(3)$ Å $\beta = 90°$	$b = 6.767(6)$ Å $\beta = 94.602(13)°$
$c = 12.298(3)$ Å $\gamma = 90°$	$c = 21.007(18)$ Å $\gamma = 90°$
V = 937.3(4) Å^3	V = 1681(3) Å^3
Z = 4	Z = 4
$D_x = 1.588$ Mg/m^3	$D_x = 1.451$ Mg/m^3
M = 4.342 mm^{-1}	M = 2.461 mm^{-1}
$F_{000} = 456$	$F_{000} = 768$
Crystal size 0.36 × 0.25 × 0.21 mm	Crystal size 0.32 × 0.28 × 0.22 mm
$\theta = 3.31$–$24.99°$	$\theta = 1.95$–$25.50°$
Reflns collected/unique = 4794/1653	Reflns collected/unique = 3282/1378
GOF on $F^2 = 1.019$	GOF on $F^2 = 1.113$
$R1 = 0.0295$, $wR2 = 0.0610$	$R1 = 0.0616$, $wR2 = 0.1834$
$R1 = 0.0358$, $wR2 = 0.0626$	$R1 = 0.1074$, $wR2 = 0.2831$
largest residuals (e Å^{-3}) = 0.411/−0.295	largest residuals (e Å^{-3}) = 0.751/−0.748

determined single crystal structures show that there is difference in the form of hydrogen bonds. In order to differentiate easily these two crystals with similar shape and color after rapid recrystallization, FT-IR and FT-Raman spectra were measured and compared. In addition, the thermal stabilities were also analyzed on the basis of different crystal structure.

2. Experimental

2.1. Preparations of CMPRHBr-I and CMPRHBr-I

Strictly followed the previously reported method [12] 1-carboxymethyl-1-methylpyrrolidinium bromide (CMPRHBr-I) was prepared. *N*-methylpyrrolidine (5 mmol) and bromoacetic acid (5 mmol) were stirred at room temperature up to solidification, and the crude product were dissolved in acetonitrile-methanol (v:v = 5:1) mixture for recrystallization. The colorless block single crystals were collected and dried in vacuum oven (yield, 85%, m.p. 179 °C). The elemental analysis (% calculated/found) was C, 37.51/37.63; H, 6.30/6.42; O, 14.28/14.34; N, 6.25/6.18.

For preparation of CMPRHBr-II, under stirring conditions, ammonia solution was added to the CMPRHBr-I (0.2241 g) aqueous solution to adjust the pH value > 8. The mixture was then slowly evaporated at room temperature, and colorless transparent block crystals of CMPRHBr-II were isolated by filtering after two weeks (yield, 73%, m.p. 149 °C). The elemental analysis (% calculated/found) was C, 45.78/45.87; H, 7.41/7.62; O, 17.42/17.23; N, 7.63/7.45.

Table 2
Experimental parameters of O—H···O and short C—H···O (Br) hydrogen bonds (Å and °) for CMPRHBr-I and CMPRHBr-II.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
CMPRHBr-I				
O(1)–H(1)…Br(1)	0.81(3)	2.33(3)	3.137(3)	176(4)
C(2)–H(2A)…O(2)^{i}	0.97	2.59	3.338(5)	134
C(6)–H(6A)…Br(1)^{i}	0.97	2.87	3.798(3)	161
CMPRHBr-II				
O(1)–H(1D)…O(1)	1.20	1.20	2.400(15)	180
C(6)–H(6A)…O(2)^{ii}	0.96	2.35	3.208(16)	149
C(5)–H(5A)…Br(1)^{iii}	0.97	2.82	3.745(12)	160

Symmetry code: i; −1 + x,y,z; ii = 3/2 − x, −1/2 − y, 2 − z; iii = x, −1 + y,z.

For the mutual transformation, a typical process is as follow: In aqueous solution of CMPRHBr-II, HBr solution was add to adjust the pH value to 5.7. The mixture was then slowly evaporated at room temperature, and colorless block crystals of CMPRHBr-I were isolated by filtering after one week (yield, 80%). The final structure was confirmed by Powder X-ray diffraction.

2.2. Experimental Characterization

Diffraction data were collected on an Agilent Technologies SuperNova dual diffractometer with an Atlas detector and Mo/Kα radiation (λ = 0.71073 Å). The crystal was kept at 296 K during data collection using

Table 3
Selection bond lengths (Å), bond and torsion angles (°) for CMPRHBr-I and CMPRHBr-II.

CMPRHBr-I		CMPRHBr-II			
Bond lengths		Bong lengths			
O2-C7	1.192(8)	N1-C1	1.57(4)	N1′-C1′	1.53(5)
O1-C7	1.311(8)	N1-C5	1.49(3)	N1′-C5′	1.40(3)
N1-C6	1.487(9)	N1-C4	1.53(3)	N1′-C4′	1.53(3)
N1-C4	1.516(10)	N1-C6	1.50(3)	N1′-C6′	1.51(3)
N1-C1	1.484(9)	O1-C7	1.29(6)	O1′-C7′	1.36(5)
N1-C5	1.500(11)	O2-C7	1.21(5)	O2′-C7′	1.12(5)
C7-C6	1.504(9)	C1-C2	1.46(4)	C1′-C2′	1.52(4)
C3-C4	1.528(11)	C2-C3	1.38(3)	C2′-C3′	1.58(3)
C3-C2	1.465(11)	C3-C4	1.64(3)	C3′-C4′	1.39(3)
C1-C2	1.497(12)	C5-C7	1.58(5)	C5′-C7′	1.55(5)
CMPRHBr-I		CMPRHBr-II			
Bond angles		Bond angles			
C4-N1-C6	108.9(5)	C5-N1-C1	108.1(19)	C5′-N1′-C1′	109(2)
C1-N1-C6	112.3(5)	C4-N1-C1	96(2)	C4′-N1′-C1′	96(2)
C1-N1-C4	102.1(5)	C4-N1-C5	108.9(18)	C4′-N1′-C5′	109.6(17)
C5-N1-C6	112.0(6)	C6-N1-C1	121(2)	C6′-N1′-C1′	117.9(19)
C5-N1-C4	109.9(6)	C6-N1-C5	111(2)	C6′-N1′-C5′	114(2)
C5-N1-C1	111.3(6)	C6-N1-C4	110.9(18)	C6′-N1′-C4′	108.4(19)
O1-C7-O2	125.1(7)	C2-C1-N1	105(2)	C2′-C1′-N1′	109(2)
C6-C7-O2	125.2(7)	C3-C2-C1	116.1(19)	C3′-C2′-C1′	102.4(17)
C6-C7-O1	109.7(6)	C4-C3-C2	93.4(17)	C4′-C3′C2′	99.7(18)
C7-C6-N1	114.9(6)	C7-C5-N1	116(2)	C7′-C5′-N1′	113(2)
C2-C3-C4	105.8(8)	C3-C4-N1	103.1(17)	C3′-C4′-N1′	107.6(18)
C3-C4-N1	102.5(6)	O2-C7-O1	128(4)	O2′-C7′-O1′	124(5)
C2-C1-N1	104.7(6)	C5-C7-O1	111(4)	C5′-C7′-O1′	107(3)
C1-C2-C3	107.4(7)	C5-C1-O2	120(4)	C5′-C1′-O2′	129(5)
CMPRHBr-I		CMPRHBr-II			
Torsion angles		Torsion angles			
N1-C1-C2-C3	26.8(5)	C5-N1-C1-C2	−138.7(13)	C5′-N1′-C1′-C2′	137.1(14)
N1-C6-C7-O1	−173.8(3)	C6-N1-C1-C2	92.3(17)	C6′-N1′-C1′-C2′	−90.5(18)
N1-C6-C7-O2	5.9(5)	C4-N1-C1-C2	−26.7(14)	C4′-N1′-C1′-C2′	23.9(17)
C1-N1-C4-C3	38.8(4)	N1-C1-C2-C3	−6.(2)	N1′-C1′-C2′-C3′	2.5(19)
C1-N1-C6-C7	177.4(3)	C1-C2-C3-C4	33.0(18)	C1′-C2′-C3′-C4′	−31.2(18)
C1-C2-C3-C4	−2.4(5)	C6-N1-C5-C7	55.5(15)	C2′-C3′-C4′-N1′	50.3(17)
C2-C3-C4-N1	−22.7(5)	C4-N1-C5-C7	178.0(11)	C5′-N1′-C4′-C3′	−160.7(14)
C4-N1-C1-C2	−40.6(4)	C1-N1-C5-C7	−78.9(15)	C6′-N1′-C4′-C3′	74.6(17)
C4-N1-C6-C7	64.6(4)	C5-N1-C4-C3	158.2(12)	C1′-N1′-C4′-C3′	−47.4(17)
C5-N1-C1-C2	76.3(4)	C6-N1-C4-C3	−79.5(15)	C6′-N1′-C5′-C7′	−60.2(16)
C5-N1-C4-C3	−77.2(4)	C1-N1-C4-C3	46.7(13)	C1′-N1′-C5′-C7′	74.1(17)
C5-N1-C6-C7	−61.1(4)	C2-C3-C4-N1	−49.8(15)	C4′-N1′-C5′-C7′	178.5(13)
C6-N1-C1-C2	−160.5(3)	N1-C5-C7-O2	26.(2)	N1′-C5′-C7′-O2′	−19.(3)
C6-N1-C4-C3	156.3(3)	N1-C5-C7-O1	−169.1(13)	N1′-C5′-C7′-O1′	166.4(13)